Effects of Substituents on the Length of Central C(sp^3)–C(sp^3) Bond in Anthracene Photodimers and Related Molecules

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Effects of substituents on the lengths of the central C–C single bond in the butterfly-shaped anthracene photodimers (**1**)—(**7**) and lepidopterenes (**8**) are studied. *X*-Ray analysis of the photodimer (**10**) of 9,10-difluoroanthracene gave a C(9)–C(10′) bond length of 1.631(3) Å. An attempt to re-determine molecular structure of the photoisomer (**5**) of [2.2](9,10)anthracenophane (**12**) by neutron diffraction analysis is also reported [C(9)–C(10′): obs. 1.64(1), calc. 1.63(1) Å]. The D_2 structure that had been proposed for the minimum-energy conformation of (**5**) is questioned and the D_{2h} symmetric conformation is suggested on the basis of the diffraction results and MNDO calculations. The experimentally determined distances of the long central C–C bonds in these butterfly compounds including dianthronyl (**9**) are well reproduced by MNDO calculations with a standard deviation of 0.013 Å. Small but significant further elongation of the central C–C bond by up to 0.07 Å resulting from annulation of cyclobutane or cyclopentane ring in anthracene photodimers and from remote chlorine substitution in lepidopterene are interpreted in terms of the increased $\pi \rightarrow \sigma^*$ orbital interation.

Anthracene photodimers (**1**)—(**7**),† lepidopterenes (**8**), and dianthronyl (**9**) have an interesting structural feature in common: each molecule contains at least one very long C(sp^3)–C(sp^3) bond exceeding 1.6 Å. Long bonds are generally reactive,[1] and the ready cleavage of the long central bonds in (**1**)—(**8**) has aroused considerable interests from diverse areas.[2–7] Although many investigators have assumed that steric repulsions between the two ring systems are responsible for the unusual lengthening of the central bond in these molecules, recent work has demonstrated that steric factors are not as important but the through-bond interaction among four aromatic rings aligned almost perpendicular to the C–C bond is responsible.[1,8,9] Among a number of possibilities, $\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ interactions destabilize and elongate the mediating C–C bond. A quantitative perturbational MO study has indicated that the former type dominates over the latter.[8]

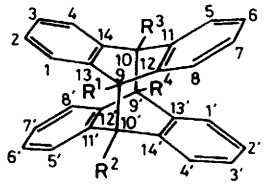
It seems interesting to investigate further the relationship between the strength of these orbital interactions, the length of mediating bond, and the chemical consequences like reactivity.[1] In this paper we examine the effect of substituent on the central bond length of butterfly compounds. We were intrigued by the extraordinarily long bond [1.77(1) Å]‡ reported for biscyclobutano-derivative (**5**),[10] a photoisomer of [2.2](9,10)-anthracenophane (**12**) (Table 1). Dunitz[12] has suggested the possibility of forming (**5**) by no-bond structures like (**13**).§ Since the stated instability of (**5**)[10] might indicate some damage to the crystal by *X*-ray irradiation, we undertook neutron diffraction analysis of this compound. Although the resultant structure could not be satisfactorily refined, this attempt furnished new information. A closer examination of the reported central bond lengths listed in Table 1 reveals that not only four-membered rings but also a five-membered ring produce enhanced lengthening of the central bond when fused to it. The effect is best illustrated with (**6**), where the C(9)–C(10′) bond [1.669(4) Å] fused with a cyclopentane ring is considerably longer than the unsubstituted C(10)–C(9′) bond [1.597(4) Å].[4] A similar difference is also apparent in (**7**). These and other effects are analysed later in this paper.

It would be interesting to be able not only to increase but also to decrease a bond length. One of us had predicted,[8] based on MINDO/3 and EHT calculations, that fluorine may strongly diminish the bond-elongating orbital interaction when attached at the bridgehead position of (**1**). In order to check the prediction, we have determined the molecular structure of 9,9′,10,10′-tetrafluoro-(**1**) [≡ (**10**)].

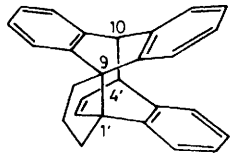
Results

X-Ray Crystallographic Analysis of Molecular Structure of (**10**).—Structural details very similar to those of (**1**) are obtained, *i.e.* two anthracene molecules are each folded at the line connecting C(9) and C(10) and united like two facing butterflies, producing D_{2h} molecular symmetry. The central bond distance of C(9)–C(10′) is found to be 1.631(3) Å, very long but comparable with most of the corresponding distances of other butterfly compounds listed in Table 1. Hence the previous MINDO/3 calculations proved incorrect. We therefore subjected (**10**) to MNDO calculation[13] and observed that this defect of MINDO/3 has been amended in the MNDO scheme (Table 1).[13a] Computed results are discussed later. We have so

† Anthracene photodimer (**1**) is the oldest known photoadduct, I. Fritzsche, *J. prakt. Chem.*, 1866, **101**, 337.
‡ Still longer C–C bonds are known: C. Gatti, M. Barzaghi, and M. Simonetta, *J. Am. Chem. Soc.*, 1985, **107**, 878.
§ Note that the structure (**13**) is different from (**12**) in that the central rings are bent in the former but planar in the latter.



	R^1	R^2	R^3	R^4
(1)	H	H	H	H
(2)	CH_3	H	CH_3	H
(3)	CHO	H	H	CHO
(4)	CH_2CH_2		H	H
(5)	CH_2CH_2		CH_2CH_2	
(6)	$CH_2CH_2CH_2$		H	H
(10)	F	F	F	F



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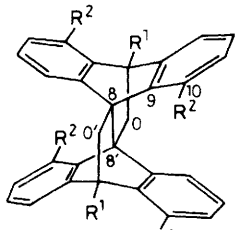
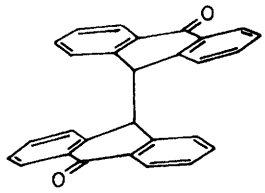


(8)

	R^1	R^2
a	H	H
b	CH_3	H
c	H	Cl



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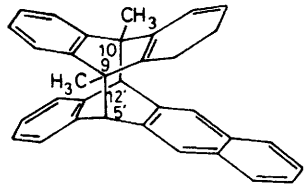

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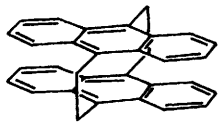

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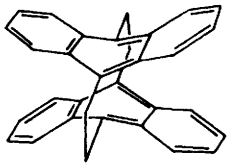

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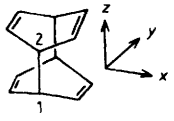

(14)

(15)

far been unable to find any example of shortened or even normal distance in the central bond of butterfly compounds.*

Neutron Diffraction Analysis of Molecular Structure of (5).—A large (6.3 mm^3) colourless single crystal of (5) was grown successfully as described in the Experimental section, but the crystal had transformed into orange [2.2](9,10)anthracenophane (12)[14] during shipment from West Germany to the U.S.A. where the neutron diffraction study was performed. On exposure to light, most (12) appeared to have reverted to the photoisomer (5), but the transformation might not have been completed as evidenced by the persistent light yellow colour in the inside of the crystal. Probably for this reason, the reflection intensities were generally weak and only 900 observable intensities out of 1 875 reflections could be collected. All other known photoisomers of [2.*n*](9,10)anthracenophane (n = 2—5) are unstable and none of them has ever been successfully analysed by diffraction methods.[4,5]

Since we are primarily interested in the carbon framework involving the C(9)–C(10′) bond, anisotropic thermal parameters were assigned to carbon atoms, and isotropic factors to hydrogen atoms. The final R factor dropped to 9.5%. The structure of the carbon skeleton had approximate D_{2h} symmetry with reasonable structural parameters including the C(9)–C(10′) bond length of 1.64(1) Å. It compares favourably with the value calculated by MNDO[13] as described below.

Molecular Mechanics Calculations.—It has been repeatedly shown that molecular mechanics[15] grossly underestimates the distances of central bonds in the butterfly compounds[8] and in the related systems,[9,16,17] providing a strong indication for the operation of factors other than steric repulsion in the bond elongation. Our MM2′ calculations[18] (Table 1, two right-hand-side columns) confirm this point.

Dunand *et al.*[4,5] have proposed, based on molecular mechanics calculations,† that the most stable conformation of (5) is of D_2 symmetry (twisted about the short molecular axis). MM2′ calculations again confirm their results. Furthermore, two-bond driver calculations[20] indicate that a pair of D_2 conformers enantiomerize into each other *via* a barrier of D_{2h} symmetric structure, which has 24.3 kJ mol^{-1} higher steric energy than the D_2 minima. Comparison of energy terms between these conformations reveals that the differences in the bending strain (D_{2h} is favoured over D_2 by 35.6 kJ mol^{-1}) and the torsional strain (D_2 favoured than D_{2h} by 36.4 kJ mol^{-1}) cancel each other and that the difference in the long-range non-bonded interaction energies (higher in D_{2h} by 19.2 kJ mol^{-1}) is primarily responsible for the barrier height. The latter difference is completely accounted for by *eight* pairs of close contact between methylene hydrogen and *peri* hydrogen in the D_{2h} conformation. However, in view of the recent recognition that the current molecular

* Shortened C–C bonds are rare, and occasionally the reported examples are suspect.[1]

† They used MMPI,[19] which gave a central bond length of 1.651 Å for (5), in surprisingly good agreement with our results (Table 1). The agreement is, however, an artifact since MMPI does not take the through-bond interaction into accounts.

mechanics force fields still use too hard hydrogen atoms,[21,22] it is highly likely that the repulsive energies of these contacts are overestimated. In that case, the calculated energy difference between D_{2h} and D_2 conformations may well be an artifact. In order to obtain more information about this point, we performed an MNDO calculation on (**5**).

MNDO Calculations.—When the D_2 conformer of (**5**) was subjected to re-optimization with MNDO, the structure changed into D_{2h} symmetry. Hence, in contrast to MM2′, the D_{2h}-symmetric structure is an energy minimum in the MNDO energy hypersurface. Close inspection of the resulting equilibrium structure revealed a remarkable feature in the way the molecule chose to relieve the repulsive strain between methylene hydrogen and *peri* hydrogen of the D_{2h} structure: the H–C–H angle in the methylene group is closed to 105.2° leading to a 1,3 H–H distance of only 1.75 Å. While this MNDO result may or may not be true, the recent realization that non-bonded hydrogens can approach closer [to 1.617(3) Å][21] than had been presumed prompts us to suggest that the absorption of strain at the cost of a decreased H–C–H angle might have been overlooked in organic stereochemistry.* It should be remembered that the two preliminary diffraction analyses of (**5**) mentioned above have indicated D_{2h} symmetry.†

The above argument would have been less persuasive if MNDO did not reproduce the known structural features of other butterfly compounds. Actually, it did. For example, the observed and calculated distances of central bonds in (**1**)—(**10**) are compared in Table 1. Excluding (**5**), we obtained a standard deviation of 0.013 Å for the errors in the MNDO distances of these bonds. This value is comparable to the mean absolute error (0.012 Å) of MNDO for a set of 58 C–C bonds reported by Dewar and Thiel.[23] MNDO generally underestimates the central bond length of butterfly compounds, except for the fluorine-substituted bond of (**10**), which is overestimated. This latter tendency has already been mentioned.[24] For other systems as well, MNDO has performed quite well in reproducing the observed C–C bond lengths undergoing elongation by the through-bond coupling.[1,9,16] In this regard, we consider the MNDO-calculated C(9)–C(10′) distance of 1.63 Å of (**5**) as quite a reliable measure, which as stated above agrees well with our tentative results from neutron diffraction.

Discussion

The central bond lengths of butterfly compounds (Table 1) range from 1.60 to 1.67 Å. This range of difference (0.07 Å) is, however, significant compared to the standard deviations in experimental determinations (<0.01 Å) and calculations (0.013 Å). In the following discussion, effects of substituents on these small changes are analysed in some detail.

Analysis of STO-3G Molecular Orbitals of Model Structures.—We first analyse *ab initio* STO-3G molecular orbitals of small molecules, *p,p′*-dibenzene (**14**)‡ and its biscyclobutano-derivative (**15**),§ which model (**1**) and (**5**), respectively,¶ in order to examine the low-lying virtual orbitals and high-lying occupied orbitals (Figure). Compound (**14**) was the subject of the previous quantitative PMO analysis[8] and the Figure provides a different view of the previous results. Orbitals with A_x symmetry‖ have nodes at the central bonds, and hence are not involved in the through-bond coupling. Among the orbitals with S_x symmetry depicted in the Figure (SSS, SAS, and SSA), the unoccupied SAS and SSA orbitals are capable of destabilizing the central bond by endowing antibonding character. The highest of the occupied SSA orbitals is essentially pure π, while the lowest empty SSA is pure σ*. The depicted levels of these two MO's are actually the results of the π→σ* interaction. Similarly, the two SAS levels represent the results of σ→π* interaction.

Comparison among the oribitals of the same symmetry between (**14**) and (**15**) reveals that, in the latter, the highest occupied SAS level is increased while the lowest unoccupied SSA level decreased as the result of annulation of the cyclobutane ring. Both these changes in (**15**) *increase* the σ→π* and π→σ* interactions, respectively. These are the reason for the longer calculated central bond distance of (**15**) compared to (**14**), and probably also the reason for the observed difference in the central bond distances between (**1**) and (**5**). However, at this point it is difficult to know the relative importance of these two interaction types.

Assessment of Relative Importance between the Two Bond-lengthening Orbital Interaction Types.—In order to simplify discussion, we consider here only the photodimers of anthracenes (**1**)—(**7**) and (**10**). Since these molecules are substituted only at the bridgehead positions, we need to consider only the energy levels of appropriate σ_{C-C} and σ^*_{C-C} orbitals, π and π* levels remaining practically unaffected by the remote substitution. We have taken the C–C bond of substituted ethanes as models of the central bond of butterfly compounds and studied their hightest σ_{C-C} and the lowest σ^*_{C-C} levels as measures of the strength of through-bond interactions. Regarding the highest σ_{C-C} orbital energies, the assigned photoelectron ionization potentials are available.[26] In order to estimate the lowest σ^*_{C-C} levels, we have performed *ab initio* STO-3G calculations of substituted ethanes at fixed geometries. Orbital energies thus collected are summarized in Table 2, where the enthanes are listed from top to bottom roughly in the increasing order of the central bond lengths of the photodimers, to which the ethanes are modelled. $E(\sigma^*_{C-C})$s (the right-hand-side column) decrease in this order and hence the π→σ* interaction must be enhanced in this order. However, IP(σ_{C-C}) values do not correlate with the increasing order of central bond lengths. Therefore, it is likely that the σ→π* interaction is much less important compared with the π*→σ type. These observations are in agreement with the previous conclusions from PMO theory.[8]

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* Among a few methylene geometries that have been reported with precisions sufficiently high to assess the present proposal, none was under repulsive constraints from outside the protons. See, however, footnote 26 of ref. 21.

† Note that averaging of nuclear positions between an enantiometric pair of D_2 conformations does not produce structural parameters relevant to D_{2h} symmetry. Hence the possibility of libration between a D_2 pair as an alternative explanation for the observed D_{2h} symmetric structure is unlikely. We thank Dr. F. Imashiro for this suggestion.

‡ Tricyclo[4.2.2.2^{2,5}]dodeca-3,7,9,11-tetraene, unknown.[8,25] For derivatives: (*a*) 3,4;7,8-dibenzo, F. C. De Shryver, K. Demeyer, and S. Toppet, *Macromolecules*, 1983, **16**, 89; (*b*) 3,4;9,10-dibenzo, Y. Tobe, F. Hirata, K. Nishida, H. Fujita, K. Kimura, and Y. Odaira, *J. Chem. Soc., Chem. Commun.*, 1981, 786.

§ Pentacyclo[8.2.2^{1,4}.2^{7,10}.0^{1,10}.0^{4,7}]hexadeca-2,8,13,15-tetraene, unknown. Labile 2,3;8,9-dibenzo derivatives have been characterized: G. Kaupp and I. Zimmermann, *Angew. Chem.*, 1976, **88**, 482; N. E. Blank and M. W. Haenel, *Chem. Ber.*, 1981, **114**, 1531.

¶ Complete optimization of carbon positions gave the following, expectedly long, central bond distances: (**14**), C(1)–C(2), 1.609 Å; (**15**), C(1)–C(10), 1.623 Å.

‖ The same symmetry designation as previously used[8] is adopted here. Three mirror planes m_x, m_y, and m_z are defined perpendicular to the *x*, *y*, and *z* axes [see structure (**14**) and Figure]. Orbitals are either symmetric (*S*) or antisymmetric (*A*) with respect to a mirror plane. Thus, S_x means that the MO is symmetrical with respect to m_x plane. $S_xS_yA_z$ is abbreviated to SSA.

Table 1. Observed and calculated lengths (Å) of unusually long bonds in butterfly compounds

Compound	Bond	Obs.[b]	Calc.[a] MNDO	diff.	MM2′	diff.
(1)	C(9)–C(10′)	1.624(3)[c]	1.585	−0.039	1.552	−0.072
(2)	C(9)–C(10′)	1.628(2)[d]	1.604	−0.024	1.562	−0.066
(3)	C(9)–C(10′)	1.61(1)[e]	1.600	−0.01	*f*	
(4)	C(9)–C(10′)	1.642(3)[g]	1.635	−0.039[h]	1.581	−0.080[h]
	C(10)–C(9′)		1.581		1.549	
(5)	C(9)–C(10′)	[1.77(1)][i]	1.632	[−0.14]	1.578	[−0.19]
		1.64(1)[j]		(−0.01)		−0.06
(6)	C(9)–C(10′)	1.669(4)[k]	1.639	−0.030	1.584	−0.085
	C(10)–C(9′)	1.597(4)[k]	1.580	−0.017	1.546	−0.051
(7)	C(9)–C(1′)	1.644(2)[l]	1.638	−0.006	*f*	
	C(10)–C(4′)	1.605(3)[l]	1.583	−0.022		
(8a)	C(8)–C(8′)	1.642(4)[m]	1.645	0.003	1.586	0.056
(8b)	C(8)–C(8′)	1.637(6)[n]	1.623	−0.014	1.580	−0.057
(8c)	C(8)–C(8′)	1.658—1.670(8)[n,o]	1.661	−0.005[p]	*f*	
(9)	C(10)–C(10′)	1.60[q]	1.584	−0.02	*f*	
(10)	C(9)–C(10′)	1.631(3)[r]	1.663	0.032	*f*	
				Std dev 0.013		

[a] See Experimental section for details. diff. = calc. − obs. [b] *X*-Ray analysis unless otherwise noted, [c] C. S. Choi and P. L. Marinkas, *Acta Crystallogr.*, 1980, **B36**, 2491. [d] Average distance of two central bonds in anthracene-tetracene photoadduct (**11**): J. Ferguson, A. W.-H. Mau, and P. O. Whimps, *J. Am. Chem. Soc.*, 1979, **101**, 2363. [e] Ref. 11*a*. [f] MM2′ has not been parameterized for these functionalities. [g] Two different bond distances not distinguished: B. F. Anderson, J. Ferguson, M. Morita, and G. B. Robertson, *J. Am. Chem. Soc.*, 1979, **101**, 1832. [h] Calculated values are averaged. [i] Ref. 10. [j] Result of preliminary neutron diffraction analysis in this work. [k] Ref 4. [l] J. Ferguson, A. W.-H. Mau, and P. O. Whimps, *J. Am. Chem. Soc.*, 1979, **101**, 2370. [m] Stable phase: P. J. Gaultier, C. Hauw, and H. Bouas-Laurent, *Acta Crystallogr.*, 1976, **B32**, 1220. [n] Ref. 29. [o] Three crystal modifications are analysed. [p] Difference from the average of three observed values (1.666 Å). [q] Standard deviation between 0.004 and 0.006 Å: ref. 11*b*. [r] This work.

Table 2. Ionization potentials of the highest σ_{C-C} orbitals and calculated energy level of the lowest σ^*_{C-C} orbitals in substituted ethanes XCH_2CH_2Y

X	Y	Modelled for	eV IP(σ_{C-C})[a]	$E(\sigma^*_{C-C})$[b]
H	H	**(1)**,**(9)**	(13.5)[c]	18.713
CH_3	H	**(2)**		17.753
CH_3	CH_3		11.09	
CH_3	C_2H_5		10.93	
F	H		12.87	
F	F	**(10)**		17.433
$-(CH_2)_2-$		**(4)**,**(5)**		16.114
$-(CH_2)_3-$		**(6)**,**(7)**	11.82	15.722
$-(CH_2)_4-$			10.32	

[a] Ionization potential data from He[I] photoelectron spectra and *ab initio* assignments are taken from ref. 26. [b] STO-3G results. All ethanes are eclipsed, with C–C = 1.538, C–H = 1.086 Å, H–C–C = X–C–C = Y–C–C = 110.71°. Substituents have standard geometrical parameters. Cyclic structures have D_{nh} symmetry and C–C = 1.538 Å. [c] Inaccurate due to severely overlapped spectrum. *Ab initio* 6-31G calculations without and with CI gave 13.84 and 12.70 eV, respectively.[26]

Why Ring-fusion Enhances Lengthening of the Central Bond.—Concentrating on the changes of $E(\sigma^*_{C-C})$, we note that the substitution with methyl and fluorine lowers the energy levels* only to small extents, consistent with the observed trend in central bond lengths, namely those of (**2**) and (**10**) are only marginally longer than that of (**1**). So far, Table 2 gives no inconsistency. The steady decrease in $E(\sigma^*_{C-C})$ which occurs upon increasing chain length of an alkane has been noted before.[27] However, $E(\sigma^*_{C-C})$ values of small cycloalkanes (Table 2) are much lower in energy than those of linear alkanes, and this is a consequence of the fact that σ bonds are cyclically delocalized in much the same manner as cyclic conjugated π bonds.[28] These results suggest greater π→σ* interaction in the ring-fused photodimers and hence longer bonds compared with acyclic-substituted photodimers. From Table 2, it is also clear that a cyclopentane ring is more effective than a cyclobutane in elongating the central bond of (**1**) when fused to it. Hence the angle strain arising from a four-membered ring does not appear to affect the σ^*_{C-C} level. In other systems, it has been shown that accumulation of angle strain leads to an increased through-bond interaction.[1,9,16]

Effects of Formyl and Chloro Groups.—The effect of a formyl group on the length of central bond of (**3**) is unremarkable (Table 1), which might appear surprising since the formyl group could be an additional source of π-electrons for the through-bond interaction. For the bond-lengthening orbital interaction to take place the formyl plane must be nearly perpendicular to the C(9)–C(10′) bond. In the crystalline state, however, the formyl plane of (**3**) is almost parallel to the central bond [C(10′)–C(9)–C=O dihedral angle 5.5°],† and hence its π-electrons are not available for interaction. Even when the carbonyl group was fixed at the most favourable orientation in a polycyclic cage structure, the bond-elongating effect was insignificantly small.[9] The low energy level as well as the small coefficient at the carbon atom of the highest occupied π-orbital of a carbonyl group are suggested as the reason for the poor interaction.[9]

Becker[29] has noted that chlorine substitution (R^2) in

*Lowering of the highest σ_{C-C} level upon fluorine substitution has been expected: C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, *J. Am. Chem. Soc.*, 1972, **94**, 1451; C. R. Brundle, M. B. Robin, and N. A. Kuebler, *ibid.*, p. 1466; E. Heilbronner and J. P. Maier, *Helv. Chim. Acta*, 1974, **57**, 151.

†Calculated from the atomic co-ordinates given in ref. 11*a*. In the MNDO-optimized structure of (**3**), this angle is 1.2°. During our recalculation of *X*-ray structure of (**3**), we noted that the C(12)–C(9)–C=O dihedral angle is 115.2°, instead of the literature[11a] value of 85°30′.

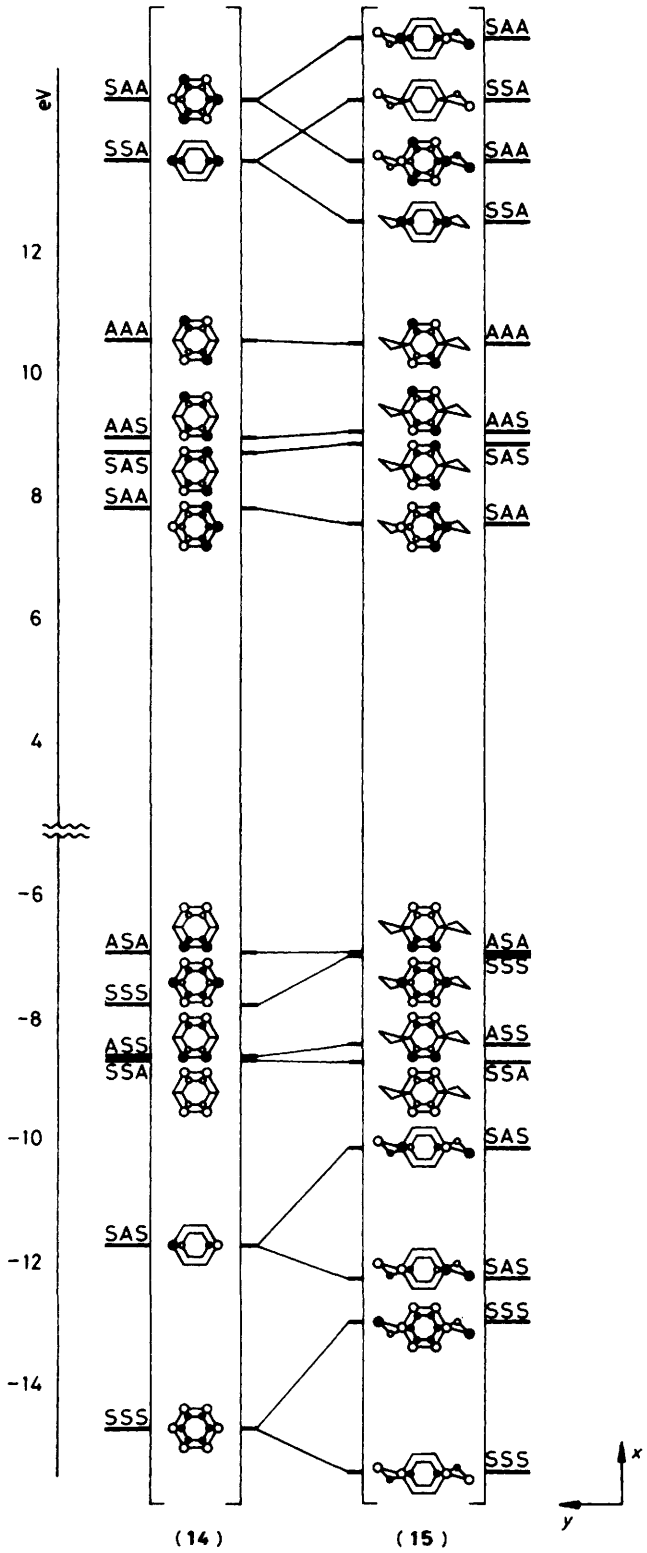

Figure. Selected molcular orbitals of model molecules (**14**) and (**15**). Only p_z orbitals as viewed down from the positive end of z-axis are drawn with the atomic orbital contribution in three categories: large, medium, and small to zero. This information as well as orbital energy levels (eV) are obtained by STO-3G calculations involving geometry optimization. Note the discontinuity in the abscissa near the zero energy level. The energy scale for the two highest vacant π orbitals of (**14**) and for the four highest vacant π orbitals of (**15**) is arbitrary

lepidopterene elongated the length of the C(8)–C(8′) bond from 1.64 in (**8a**) to 1.67 Å in (**8c**). Two factors are considered as responsible. First, a pair of close contacts between chlorine [at C(10) and C(10′)] and methylene protons cause considerable angle deformations at the quaternary carbon [C(8) and C(8′)].* Such strain is known, in other systems, to enhance bond lengthening by the through-bond mechanism by lowering the σ* level.[6,9,16] Second, π-donating chlorine atoms should increase the highest occupied π-orbital level of the benzo group, and this effect also strengthens the π→σ* interaction. It is interesting to note that the chlorine atom attached at a remote position appears to contribute more effectively than the fluorine atom attached directly with regard to the elongation of the central bond.

Conclusions.—(1) The central C–C bond length of tetrafluoro-derivative (**10**) of the anthracene photodimer [C(9)–C(10′) 1.631(3) Å] was obtained by *X*-ray analysis, and proved comparable to those of other bridgehead-substituted anthracene photodimers.

(2) Attempted neutron diffraction analysis of a single crystal of (**5**) could not be brought to completion due to partial cycloreversion. However, the best possible guess for the central bond length [C(9)–C(10′) 1.64(1) Å] was obtained.

(3) The possibility of a D_2 structure for the minimum-energy conformation of (**5**), previously proposed on the basis of molecular mechanics calculation, is questioned, in view of the recently recognized overestimation of H–H non-bonded interactions in molecular mechanics schemes. MNDO calculations suggest that the minimum-energy structure of (**5**) has D_{2h} symmetry.

(4) MNDO calculations reproduce well the central bond lengths of (**1**)—(**4**) and (**6**)—(**10**), with a standard deviation of 0.013 Å.

(5) Energy levels of the highest σ_{C-C} and the lowest σ^*_{C-C} may be used as measures of the extent of the bond-elongating through-bond interaction, σ→π* and π→σ*, in these photodimers. The latter was confirmed to dominate over the former.

Experimental

Single-crystal X-Ray Analysis of (**10**).—A sample was kindly provided by Professor N. C. Yang, Chicago, and crystals were grown from pyridine. The crystals were monoclinic, space group $P2_1/c$, with a = 14.796(5), b = 9.812(4), c = 13.197(5) Å, β = 93.07(3)°, Z = 4. Mo-K_α radiation was used. A total of 3 000 reflections were collected on a Syntax $P2_1$ diffractometer in a θ—2θ scan mode. A trial structure was obtained by direct methods using the program MULTAN,[30] and it was refined by full matrix, least squares using all 3 000 reflections. Data were corrected for Lorentz and polarization factors, but not for absorption. Anisotropic thermal parameters were used for C and F, and isotropic for H. The positions of the hydrogens were not refined. The final discrepancy index R was 0.044 [based on the 1 918 reflections for which $I > 3\sigma(I)$]; the real goodness-of-fit was 1.6. Final positional and thermal parameters are given in Table 3. In all details, the structure is very similar to that of the parent, anthracene photodimer (**1**).

Crystal Growing of (**5**).—Freshly distilled dichloromethane was pretreated with solid sodium and potassium carbonates for at least 2 days. Compound (**5**) (60 mg)[31] was magnetically stirred into dichloromethane (100 ml) for 2 h at room temper-

*C(0′)–C(8)–C(9) 117.9(5) to 118.3(4)° (*X*-ray), 114.9° (MNDO); Chlorine–C(10)–C(9) 124.1(4) to 125.4(4)° (*X*-ray), 126.2° (MNDO).

Table 3. Final atomic co-ordinates ($\times 10^5$ for non-hydrogen atoms and $\times 10^4$ for hydrogen atoms) and anisotropic temperature factors ($\times 10^4$) of (**10**). Estimated standard deviations are given in parentheses

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	80 597(27)	27 417(37)	24 504(32)	406(29)	459(25)	527(30)	19(20)	−93(23)	−80(21)
C(2)	83 325(27)	38 928(36)	19 410(31)	542(28)	377(24)	678(31)	−13(21)	−127(24)	−29(22)
C(3)	85 797(26)	38 183(36)	9 590(31)	552(29)	352(23)	692(31)	−65(20)	−77(24)	129(22)
C(4)	85 672(29)	25 669(36)	4 587(32)	413(32)	507(25)	483(30)	−27(20)	−90(25)	114(20)
C(5)	93 234(25)	−19 860(36)	9 416(29)	376(26)	440(23)	538(27)	−14(20)	−18(21)	−48(21)
C(6)	96 733(28)	−28 870(36)	16 779(34)	415(31)	374(23)	729(35)	15(19)	−79(27)	−15(22)
C(7)	94 223(28)	−28 060(37)	26 594(35)	427(32)	436(25)	664(35)	49(20)	−90(27)	120(22)
C(8)	88 138(26)	−18 305(37)	29 363(28)	422(27)	504(24)	488(25)	−30(22)	−62(21)	44(21)
C(9)	77 789(23)	1 773(34)	24 454(23)	420(23)	409(22)	263(21)	−15(19)	−34(17)	−20(17)
C(10)	82 834(23)	110(33)	4 676(24)	356(22)	400(22)	331(21)	−17(19)	76(17)	9(18)
C(11)	87 075(22)	−10 101(32)	12 236(25)	323(22)	350(21)	398(23)	−32(18)	−46(18)	−6(18)
C(12)	84 537(23)	−9 085(33)	22 155(25)	334(22)	371(22)	383(22)	−60(18)	−57(18)	38(18)
C(13)	80 587(23)	14 917(34)	19 512(26)	357(24)	375(22)	355(23)	−18(18)	−60(18)	−12(18)
C(14)	83 191(23)	14 029(32)	9 580(26)	320(22)	362(22)	394(24)	−13(18)	−77(19)	44(18)
C(1′)	69 561(26)	−29 987(37)	1 147(30)	411(28)	474(24)	503(27)	61(21)	−84(22)	−110(21)
C(2′)	66 827(26)	−41 421(35)	6 190(32)	526(28)	320(22)	736(30)	52(21)	−123(24)	−90(22)
C(3′)	64 249(26)	−40 503(35)	15 940(31)	511(28)	335(22)	723(31)	−34(20)	−120(24)	85(22)
C(4′)	64 427(27)	−28 027(35)	21 008(32)	370(29)	451(24)	513(30)	−33(19)	−61(24)	69(20)
C(5′)	57 145(25)	17 494(36)	15 873(28)	389(25)	453(23)	497(25)	3(21)	−39(21)	−71(21)
C(6′)	53 399(28)	26 152(35)	8 447(35)	414(32)	440(25)	680(35)	92(20)	10(27)	−9(21)
C(7′)	55 834(30)	25 003(36)	−1 419(35)	476(35)	510(27)	611(35)	124(21)	−113(28)	126(21)
C(8′)	62 020(25)	15 328(36)	−4 149(27)	442(26)	522(25)	435(24)	−7(21)	−60(20)	40(20)
C(9′)	72 528(23)	−4 342(33)	1 073(23)	420(23)	430(22)	244(20)	26(19)	6(18)	−10(17)
C(10′)	67 472(22)	−2 458(33)	20 784(23)	376(23)	369(21)	324(20)	−22(18)	78(18)	−18(17)
C(11′)	63 282(22)	7 636(33)	13 208(25)	315(22)	358(21)	425(23)	4(18)	−33(18)	−2(18)
C(12′)	65 769(22)	6 480(32)	3 323(24)	336(22)	345(20)	365(22)	−20(18)	−14(18)	−9(17)
C(13′)	69 746(23)	−17 395(34)	6 025(27)	285(23)	376(22)	437(25)	−1(18)	−30(19)	−19(19)
C(14′)	67 143(24)	−16 487(33)	15 929(26)	341(23)	372(22)	397(24)	13(19)	−52(19)	−18(19)
F(9)	77 761(13)	3 634(20)	34 944(13)	604(15)	525(13)	321(12)	−6(11)	−53(11)	−36(10)
F(10)	87 786(13)	386(19)	−3 927(13)	472(13)	563(14)	433(13)	−1(11)	104(11)	12(12)
F(9′)	72 643(13)	−6 314(19)	−9 401(14)	578(15)	546(13)	337(12)	21(12)	−42(11)	−49(10)
F(10′)	62 541(13)	−2 542(19)	29 471(14)	485(14)	511(13)	425(12)	7(11)	98(11)	17(11)

Atom	*x*	*y*	*z*	*B*
H(1)	7 866	2 807	3 168	4.0
H(2)	8 348	4 797	2 298	5.0
H(3)	8 770	4 661	599	4.9
H(4)	8 740	2 512	−266	4.0
H(5)	9 515	−2 040	222	4.0
H(6)	10 113	−3 608	1 486	4.8
H(7)	9 684	−3 459	3 183	4.6
H(8)	8 629	−1 782	3 657	4.3
H(1′)	7 143	−3 074	−604	3.8
H(2′)	6 674	−5 050	269	4.8
H(3′)	6 218	−4 888	1 951	4.7
H(4′)	6 261	−2 740	2 823	3.7
H(5′)	5 541	1 835	2 311	3.9
H(6′)	4 893	3 328	1 033	4.6
H(7′)	5 307	3 129	−672	4.6
H(8′)	6 381	1 460	−1 136	4.0

ature, filtered under gravity, irradiated with daylight until colourless, and stored in a refrigerator (4 °C) for one day. Some tiny crystals of (**5**) were pipetted onto an object slide glass, selected under a microscope, washed with fresh dichloromethane, and checked for the absence of twinning under a polarization microscope. Three of these were dropped into a hot-saturated and hot-filtered daylight- and/or roomlight-irradiated soluton (80 ml) of (**5**) in dichloromethane, which was contained in a narrow-necked Erlenmeyer flask (100 ml). This solution was placed on a running magnetic stirrer, in order to generate a slight vibration, and allowed to evaporate down to *ca.* 10 ml at room temperature for 2 days through a cover of aluminium foil with some holes in it. The three grown crystals were picked out of the conglomerate, washed and brushed in several drops of dichloromethane on an object glass by means of a small paint-brush, and treated as before. The residual crystals and solution were used for the preparation of the next saturated solution. Completely new material was used after 10 cycles for the preparation of the solution. After 25 growing cycles the largest of the three colourless single crystals had a volume of 1.2 mm^3 and after 15 more cycles it weighed 8.4 mg (6.3 mm^3). This crystal was embedded in cotton wool for shipment.

Neutron Diffraction Analysis of (**5**).—A six-sided crystal of the photoisomer bounded by three pairs of cleavage planes, (1 0 0), (0 1 1), and (0 $\bar{1}$ 1), had suffered a phase transformation to the b-form of the anthracenophane (**12**) as indicated by the characteristic colour change to bright orange.[14,31] However, by constant exposure to daylight and fluorescent light (filtered through a Pyrex glass of 5 mm thickness), the orange colour

Table 4. Carbon fractional co-ordinates ($\times 10^4$) and equivalent isotropic temperature factors (*B*) of (**5**). Estimated standard deviations are given in parentheses

Atom	*x*	*y*	*z*	*B*
C(1)	2 853(8)	−572(7)	3 492(11)	5.1(2)
C(2)	3 864(9)	−1 385(8)	3 601(14)	5.9(2)
C(3)	3 460(10)	−2 144(9)	2 287(13)	6.0(2)
C(4)	2 131(9)	−2 061(5)	1 003(11)	4.4(2)
C(5)	−2 810(7)	−1 439(6)	−174(9)	4.1(2)
C(6)	−3 786(9)	−1 199(7)	626(11)	5.1(2)
C(7)	−3 376(8)	−432(7)	1 934(12)	5.2(2)
C(8)	−2 021(8)	52(6)	2 364(9)	3.8(2)
C(9)	396(7)	317(4)	1 945(8)	2.6(1)
C(10)	−380(7)	−1 171(4)	−513(7)	2.6(1)
C(11)	−1 457(6)	−953(4)	282(7)	2.5(1)
C(12)	−1 082(8)	−186(5)	1 538(8)	3.2(1)
C(13)	1 497(6)	−527(4)	2 160(8)	2.8(1)
C(14)	1 124(7)	−1 284(5)	892(8)	2.9(1)
C(R1)	779(11)	1 214(6)	3 258(9)	4.6(2)
C(R3)	−737(11)	−2 008(5)	−1 893(10)	4.5(2)

gradually disappeared and it finally became faint yellowish with slightly darker yellow shadows in the deep interior. The crystal was mounted on a neutron diffractometer at the National Bureau of Standards reactor, and the entire diffractometer was covered with transparent acrylic plates (5 mm thick) to filter out the u.v. radiation emitted from the mercury light of the reactor hall. A preliminary examination of the crystals by neutron diffraction gave no evidence of twinning. The crystal orientation and unit cell dimensions, $a = 9.87(5)$, $b = 13.00(7)$, $c = 8.51(4)$ Å, $\beta = 111.8(4)°$ with space group $P2_1/c$, were determined by the least-squares refinements of the setting angles of 15 strong intensity reflections. A total of 4 301 reflections in an entire hemisphere were measured within the limit of 100° in 2θ angle with 1.268 Å neutrons using an automated four-circle diffractometer. The observed integrated intensities were corrected for the absorption effect by a segment integration method, using the linear absorption coefficient μ of 1.9 cm^{-1} and 8^3 integration segments. The observed data were reduced to 1 875 unique reflections by averaging the equivalent reflections. Among them only 900 reflections showed observable intensities, *i.e.* intensities greater than two times the standard deviation. All other reflections were registered as unobservable. The agreement factor between the two sets of equivalent reflection data (for *hkl* and $h\bar{k}l$), $R = \Sigma(\Delta F/F_{av})$, was 0.03, where $\Delta F = |F(hkl) - F(h\bar{k}l)|$ and $F_{av} = 0.5[F(hkl) + F(h\bar{k}l)]$.

The computer program RFINE [32] was used for the structure refinement. The initial parameters of the refinement were taken from the structure determined by Ehrenberg.[10] The residual indices of the refinements, R_w and R, were 0.103 and 0.141, respectively, with the isotropic temperature factors assigned to all atoms, where $R_w^2 = \Sigma w(\Delta F)^2/\Sigma w F_o^2$ and $R = \Sigma\Delta F/\Sigma F_o$ for $\Delta F = |F_o - F_{cal}|$. Upon assigning anisotropic thermal parameters to carbon atoms, the residual indices reduced to 0.072 and 0.095, respectively. Positional parameters of carbon atoms at this stage are given in Table 4. Hydrogen co-ordinates and anisotropic temperature factors of carbon atoms parameters are in Supplementary Publication No. SUP 56554 (4 pp.).*

Computation.—In MM2′ calculations, carbon atoms of benzene ring were given a special atom type according to the method of Allinger.[33] Parameters for cyclobutane ring were transferred from MM2[34] without change. In *ab initio* calculations, the current version of GAUSSIAN 80[35] was locally modified in order to treat such large molecules as (**14**).[36] The STO-3G basis set[37] was used, starting with MNDO- or MM2′-minimized geometries and optimizing all carbon positions by the Murtaugh–Sargent method.

* For details of the Supplemantary Publication Scheme, see Instructions for Authors (1986), *J. Chem. Soc., Perkin Trans.* 2, 1986, issue 1

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